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MONO-SUBSTITUTION OF IRON PENTACARBONYL METAL HYDRIDE. FACILITATION

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Summary

Controlling the degree of substitution of iron pentacarbonyl with neutral ligands has usually been difficult Conditions are reported whereby considerable control may be exercised over the substitution of iron pentacarbonyl, with PPh_3 the ratio of mono-/disubstitution may be varied over a range of 50 The substituted iron carbonyl complexes were obtained by treating iron pentacarbonyl with lithium aluminum hydride or sodium borohydride in refluxing THF in the presence of a variety of neutral ligands The method is particularly useful for a simple high yield synthesis for monosubstituted iron carbonyls

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Introduction

Controlling the degree of substitution of iron pentacarbonyl by neutral ligands has usually been difficult Coordinatively saturated $Fe(CO)_5$ undergoes substitution only under conditions (thermal or photochemical) which promote dissociation of CO, in general, yields are poor and mixtures of mono- and disubstituted carbonyl complexes are obtained [1-3] Synthetic routes employing the more expensive polynuclear iron carbonyls also lead to mixtures of $Fe(CO)_4L$ and $Fe(CO)_3L_2$ [1-4] The recent publication by Conder and Darensbourg [5] of a high yield photochemical synthesis for mono-substituted derivatives of iron pentacarbonyl promots us to report a simple, high yield, non-photochemical route which allows considerable control over the ratio of mono- to disubstitution

It seemed likely that a new synthetic approach might be obtained by the reversible conversion of $Fe(CO)_5$ to an intermediate capable of generating a vacant coordination site under mild conditions For example, a vacant coordination site is generated under ambient conditions by the migratory insertion of CO in the alkyl C—Fe bond of alkyl tetracarbonylferrate(0) complexes [6]. Furthermore, if conversion to the active intermediate involved nucleophilic attack on CO it might be possible to take advantage of the predicted difference in reactivity of $Fe(CO)_5$ and $Fe(CO)_4L$ toward nucleophilic attack on coordinated

CO to control the degree of substitution [7] In this context hydride ion might conceivably serve as an activator for $Fe(CO)_5$

Chatt and co-workers had previously employed sodium borohydride in refluxing alcohol to activate Group VI metal carbonyls toward substitution by neutral ligands, in this case the products obtained were usually disubstituted [8] We report here that the reaction of iron pentacarbonyl with lithium aluminum hydride or sodium borohydride in tetrahydrofuran (THF) in the presence of a variety of neutral ligands can be controlled to afford high yields of $Fe(CO)_4L$

Experimental

General information All reactions were run in Schlenk-type glassware under an argon atmosphere unless noted otherwise, no precaution was taken to exclude air or moisture during the work-up and purification of $Fe(CO)_4L$ Progress of the reactions was followed by IR spectroscopy using 0 1 mm CaF_2 cells and a Perkin—Elmer model 457 spectrophotometer THF was distilled from CaH_2 and deoxygenated prior to its use, solvents for chromatography were used as obtained from commercial sources Iron pentacarbonyl (Strem Chemical) and the liquid phosphites were distilled and stored over molecular sieve 4A The preparation given below for $Fe(CO)_4As(C_6H_5)_3$ is representative of that employed for phosphine and arsine complexes listed in Table 1 with the exception of $Fe(CO)_4P(CH_2CH_2CN)_3$, the preparation given for the triphenyl phosphite complex is representative of that employed with other phosphites

Progress of the reaction and the ratio $Fe(CO)_4L/Fe(CO)_3L_2$ were monitored by following changes of ν(CO) in the infrared spectrum Beer's law plots for $Fe(CO)_4P(C_6H_5)_3$ and $Fe(CO)_3[P(C_6H_5)_3]_2$ in CH_2Cl_2 revealed that the extinction coefficients for the *E* mode of $Fe(CO)_4L$ and the *E'* mode of $Fe(CO)_3L_2$ were equal ±10% The product ratios reported in this work assume this relationship between extinction coefficients holds for other pairs of mono and disubstituted iron carbonyls [9]

Complexes were identified by comparison of infrared spectra and melting points with literature values and by elemental analyses for new compounds

TABLE 1

$Fe(CO)_4L$ YIELD DATA $LiAlH_4$ PROMOTED SUBSTITUTION

L	Reaction time[a]	Yield of $Fe(CO)_4L$[b]	Ratio[c] of $Fe(CO)_4L/Fe(CO)_3L_2$
$(C_6H_5)_3P$	50	60	10
$(p\text{-}CH_3C_6H_4)_3P$	17	70	8
$(NCCH_2CH_2)_3P$	22	60	8 4
$(C_2H_5O)_3P$	22	55	8
$(C_6H_5O)_3P$	72	38	5
$(C_6H_5)_3As$	41	68	14
$(C_6H_5)_3Sb$	48	60	22

[a] Not optimized [b] Yield of isolated complex reaction scale 4 5 mmol $LiAlH_4$ 10 mmol L and 15 mmol $Fe(CO)_5$ in 70 ml THF heated in a 75°C oil bath [c] As determined from the ratio of ν(CO) see Experimental section

Preparation of $Fe(CO)_4As(C_6H_5)_3$ To 4 5 mmol of $LiAlH_4$ and 10 mmol of triphenylarsine in ca 60 ml of THF was added 15 mmol of iron pentacarbonyl The reaction mixture was stirred at 25°C for 1 h, then in a 75°C oil bath until the reaction was complete (usually 12-48 h) The progress of the reaction was monitored by following changes in the carbonyl bands (IR) Upon cooling, the suspension was filtered through a short column (3") of alumina, the column was washed with methylene chloride and the combined eluant was concentrated in vacuo to afford a yellow brown solid, 4 26 g The solid, in a minimal amount of CH_2Cl_2, was chromatographed over neutral alumina (ca 200 g, Brockman activity number 1) The column was eluted first with hexane to remove any unreacted arsine or $Fe(CO)_5$, then with 4/1 hexane/benzene which removed the desired monosubstituted product

Preparation of $Fe(CO)_4P(CH_2CH_2CN)_3$ The reaction was run as described above and the THF solution was filtered through a short (3 ') column of alumina The column was eluted with acetone and the combined eluant was concentrated in vacuo to afford a tan-brown solid Recrystallization from acetone—methanol yielded 2 20 g of off-white crystalline powder An additional recrystallization from acetone—methanol gave pale-yellow crystals, m p 190 192°C (dec), ν(CN) 2254 w, ν(CO) 2058 s, 1980 s, 1946 vs cm^{-1} Found C, 43 38, H, 3 31, N, 12 04, $C_{13}H_{12}N_3O_4PFe$ calcd C, 43 24, H, 3 35, N, 11 64%

Preparation of $Fe(CO)_4P(OPh)_3$ To 180 mg $LiAlH_4$ (4 5 mmol) in 60 ml THF was added 10 mmol of $P(OPh)_3$ and 15 mmol of $Fe(CO)_5$ The reaction mixture was stirred in a 75°C bath and a slow reaction was observed by infrared analysis After 44 h of heating, an additional 70 mg of $LiAlH_4$ was added and heating was continued to a total of 84 h The reaction product was worked up as indicated for $Fe(CO)_4AsPh_3$ The monosubstituted product was obtained in 38% yield as pale yellow needles, m p 68 69°C (lit 68 69°C)

Preparation of $Fe(CO)_3(PPh_3)_2$ To 30 mg $LiAlH_4$ and 5 0 mmol of PPh_3 in 7 ml THF was added 1 5 mmol $Fe(CO)_5$ The mixture was stirred in a 75°C bath for 12 h at which time IR analysis indicated that all of the $Fe(CO)_5$ had reacted An additional 10 mg of $LiAlH_4$ was added at 12 and at 36 h Heating was continued for a total of 50 h, at which time IR analysis indicated that most of the $Fe(CO)_4L$ had been converted to $Fe(CO)_3L_2$ The reaction mixture was poured into an open beaker and allowed to evaporate The residue was extracted with THF and H_2O was added in small amounts to the filtered extract to crystallize the product A total of 713 mg (71% yield) of yellow crystals were collected, m p 264 265°C (lit 272°C) IR analysis indicated the crystals were pure $Fe(CO)_3(PPh_3)_2$

Treatment of $Fe(CO)_5$ with $LiAlH_4$ (A) To 10 mg $LiAlH_4$ in 7 ml THF was added 1 5 mmol of $Fe(CO)_5$, the suspension was sampled periodically by IR At 25°C a weak ν(CO) appeared at ca 1910 cm^{-1} which is likely the formyl complex I On heating to 75°C a new band appeared at 1955 cm^{-1}, but its rate of appearance was much slower than that of the usual substitution reaction (Addition of PPh_3 to this solution resulted in no rapid reactions) (B) To 50 mg $LiAlH_4$ in 7 ml THF was added 1 5 mmol of $Fe(CO)_5$ The dark red suspension was sampled immediately under argon and analyzed by IR One-half to 2/3 of the $Fe(CO)_5$ had disappeared New bands appeared at 1968 m, 1932 m, 1910 m, and 1880 w-m cm^{-1} The band at 1968 increased with time

This same decomposition of $Fe(CO)_5$ was observed when the reaction was carried out as described here but with 5 0 mmol of triphenylarsine or trimethyl phosphite present

Isolation of products from treatment of $Fe(CO)_5$ with $LiAlH_4$ To 200 mg (5 mmol) of $LiAlH_4$ in 30 ml of THF under CO was added 2 5 mmol of $Fe(CO)_5$. The grey suspension darkened in color After one hour, IR analysis indicated partial conversion to the formyl complex, ν(CO) 1940, 1912, and 1565, and a small amount of the hydrido complex, ν(CO) 1880 cm^{-1} An additional 50 mg of $LiAlH_4$ was added and 0 5 h later another 100 mg was added Infrared analysis indicated that most of the $Fe(CO)_5$ had reacted, in addition to unreacted $Fe(CO)_5$ there were ν(CO) bands at 1960 (polynuclear carbonyl), 1940 (formyl), 1912 (formyl and hydrido complexes), 1880 (hydrido), and 1565 (formyl complex) Bis(triphenylphosphine)iminium chloride [10] (1 0 g, 1.75 mmol) was added to the reaction mixture along with 15 ml of methanol The solvents were evaporated in vacuo The residue was extracted under argon with CH_2Cl_2 and the extract was filtered Ether and then hexane was added to the red filtrate in small aliquots

A crop of dark red crystals, 240 mg, was obtained on standing, in addition to IR bands associated with the bis(triphenylphosphine)iminium cation there were ν(CO) (KBr) 1936 s(br), 1900 m(br), (DMF) 1925 s, 1895 m-s, and 1870 (sh) cm^{-1}. A survey of anionic polynuclear iron carbonyls reported in the literature revealed that $Fe_3(CO)_{11}^{2-}$, prepared in solution (DMF) by Edgell and co-workers [11] has a ν(CO) pattern 1941 s, 1931 m, 1884 w similar to that observed for the dark red crystals

On standing in the cold, a crop of off-white crystals deposited from the filtrate, 170 mg, IR bands in addition to those associated with the large cation were ν(CO) (KBr) 2000 w, 1908 m, and 1880 s cm^{-1}, identical to those reported earlier for $(Ph_3P)_2N[HFe(CO)_4]$ [6]

We cannot unequivocally establish the presence of the formyl complex I although infrared bands were observed in the appropriate regions (2000, 1935, 1910, and 1565 cm^{-1}) [12] The formyl complex would be both a likely product from the reaction of $Fe(CO)_5$ with hydride ion and a likely precursor to the hydrido complex which was also observed Attempts to isolate the formyl complex were unsuccessful Infrared analysis of the reaction mixture before and after the work-up procedure suggest that the formyl complex may be converted to the hydrido complex under the conditions of the work-up

Treatment of $HFe(CO)_4^-$ with L (A) To 0 21 mmol of $(Ph_3P)_2N[HFe(CO)_4]$ and 0 22 mmol of $P(CH_2CH_2CN)_3$ under argon was added 20 ml of THF. The pale yellow solution was stirred and heated in a 75°C oil bath for 2.5 days without any changes in the carbonyl region of the IR spectrum being observed $LiAlH_4$ (50 mg) was added and stirring was continued in the bath for an additional 2 5 days but still no conversion to $Fe(CO)_4L$ was observed

(B) To 1 5 mmol of $Fe(CO)_5$ in 20 ml of THF under a CO atmosphere was added 3 mmol of $LiAlH_4$, the mixture was stirred for 11 h at 25°C IR analysis of the red solution indicated a large amount of unreacted $Fe(CO)_5$ in addition to ν(CO) at 1965 (sh), 1932 m, 1910 s, and 1880 m cm^{-1} One mmol of $P(CH_2CH_2CN)_3$ was added to the reaction mixture and stirring was continued at 25°C. After 2 h most of the $Fe(CO)_5$ had been converted to $Fe(CO)_4L$ but the other bands were unchanged Another 50 mg of ligand was added and stirring was continued for 14 h after which time all of the $Fe(CO)_5$ had been converted to $Fe(CO)_4L$ but the other $\nu(CO)$ remained unchanged

Conversion of $Fe(CO)_4L$ to $Fe(CO)_3L_2$ To 10 mg $LiAlH_4$ and 1 0 mmol of PPh_3 in 7 ml THF was added 0 5 mmol of $Fe(CO)_4PPh_3$ and the reaction mixture was heated in a 75°C bath under argon After 48 h an additional 10 mg $LiAlH_4$ was added and heating was continued for an additional 20 h The reaction mixture was treated as described above, pure $Fe(CO)_3L_2$ was isolated in 44% yield

Results and discussion

Synthesis Iron pentacarbonyl does not react with triphenylphosphine in refluxing THF [1], but when a suspension of triphenylphosphine and lithium aluminium hydride or sodium borohydride in THF was treated with excess iron pentacarbonyl and heated, the corresponding monosubstituted iron carbonyl complex was formed in good yield The reaction appears to be general for a variety of neutral ligands (tertiary phosphines, phosphites, arsines, and stibines), furthermore, the reaction conditions are sufficiently mild to tolerate functional groups such as nitrile in the ligand (Table 1)

Reactions were run with the neutral ligand (L) as the limiting reagent since it is frequently the limiting material economically and excess $Fe(CO)_5$ is easily removed due to its volatility and ease of autoxidation to insoluble oxides The THF solution of reaction products was filtered through a short column of alumina to remove insoluble material and then was chromatographed on alumina to give pure $Fe(CO)_4L$ No attempt was made to isolate the small yield of $Fe(CO)_3L_2$ Yields reported in Table 1 are for isolated products obtained via $LiAlH_4$ facilitated reactions, similar yields were obtained with $NaBH_4$ $Fe(CO)_4$-$P(CH_2CH_2CN)_3$ (59%), $Fe(CO)_4AsPh_3$ (80%)

We observed an ability to control the degree of substitution which is unique for organometallic synthesis Factors effecting the ratio of mono- to disubstitution, reactions 1 and 2, will be discussed below

$$Fe(CO)_5 + L \rightarrow Fe(CO)_4L + CO \qquad (1)$$

$$Fe(CO)_4L + L \rightarrow Fe(CO)_3L_2 + CO \qquad (2)$$

Effect of concentration and type of metal hydride Metal hydrides were observed to be effective in a reasonably narrow concentration range, a characteristic which led us initially to underestimate the utility of sodium borohydride The effect of a systematic variation in $LiAlH_4$ concentration on the substitution of $Fe(CO)_5$ with PPh_3, $P(OCH_3)_3$, and $AsPh_3$ is shown in Table 2 The highest ratios of mono- to disubstitution were obtained when the concentration of $LiAlH_4$ was of the order of 0 125 mmol $LiAlH_4$/1 5 mmol $Fe(CO)_5$, although at this concentration the reaction was quite slow High ratios of mono-/disubstitution combined with optimum reaction rates (12 h versus 41 h for the conditions cited above) were obtained when 0 25 mmol $LiAlH_4$/1 5 mmol $Fe(CO)_5$ was used As the relative concentration of $LiAlH_4$ or $NaBH_4$ was increased the reaction rate increased but the ratio of mono-/disubstitution decreased

TABLE 2

EFFECT OF $LiAlH_4$ AND L CONCENTRATIONS ON THE PRODUCT RATIO[a]

$LiAlH_4$ (mmol)	L(mmol)	$Fe(CO)_4L/Fe(CO)_3L_2$[b]
0 125	1 0 PPh_3	12
0 25	1 0	9
1 25	1 0	1 6
0 25	3 0	3 7
0 50	5 0	1 3
1 25	5 0	0 2
0 25	1 0 $AsPh_3$	16
0 25	3 0	16
1 25	5 0	1 1
0 50	1 0 $P(OCH_3)_3$	3 5
0 75	5 0	1 0

[a] Run under argon with 1 5 mmol $Fe(CO)_5$ in 7 ml THF and heated in a 75°C bath [b] Ratios were read after a constant value was attained or where L was in excess at the end of 24 h The value reported is an average of at least two runs

When $Fe(CO)_5$ and ligand were treated with higher concentrations of $LiAlH_4$ (e g , 1 25 mmol $LiAlH_4$/1 5 mmol $Fe(CO)_5$), a very rapid reaction of $Fe(CO)_5$ with $LiAlH_4$ was observed (whether or not ligand was present) which resulted in conversion of approximately half of the $Fe(CO)_5$ to other carbonyl products (Accordingly, product ratios obtained at higher concentrations of $LiAlH_4$ were somewhat less accurate than ratios obtained at lower $LiAlH_4$ concentrations because of some overlap in $\nu(CO)$ of products and side-products) Yields of isolated complexes from reactions using high $LiAlH_4$ concentrations were lower than from reactions using lesser amounts of $LiAlH_4$, probably due to this initial decomposition of the $Fe(CO)_5$

A comparison of the selectivity of $LiAlH_4$ and $NaBH_4$ as substitution promoters for $Fe(CO)_5$ is reported in Table 3 Sodium borohydride was found, in all cases examined, to lead to more selective formation of monosubstituted complexes The ratios in Table 3 are consistent with our observation that the conversion of mono- to disubstituted iron carbonyl (eqn 2) was considerably slower with $NaBH_4$ than it was with $LiAlH_4$ (The rate of metal hydride facilitated monosubstitution (eqn 1) appeared to be of the same order of mag

TABLE 3

COMPARISON OF $LiAlH_4$ AND $NaBH_4$ AS SUBSTITUTION PROMOTERS[a]

L	$Fe(CO)_4L/Fe(CO)_3L_2$ obtained with [b]	
	$LiAlH_4$	$NaBH_4$
PPh_3	9	12
$AsPh_3$	14	20
$P(CH_2CH_2CN)_3$	7	>17
$P(OCH_3)_3$[c]	3 5	7

[a] Experimental conditions 10 mg metal hydride 1 0 mmol L and 1 5 mmol $Fe(CO)_5$ in 7 ml THF was heated in a 75°C bath under argon. [b] Each value represents average of at least two runs [c] With phosphites 20 mg of metal hydride was employed

nitude for $NaBH_4$ and $LiAlH_4$.) Accordingly, $NaBH_4$ was less effective than $LiAlH_4$ for promoting the synthesis of disubstituted products.

Effect of concentration and type of ligand. The effect of neutral ligands on the ratio of mono-/disubstitution is shown in Table 2. Increasing the ratio of $PPh_3/Fe(CO)_5$ favored increased disubstitution whereas increasing $AsPh_3/Fe(CO)_5$ had little effect, perhaps in response to the greater steric bulk of the $AsPh_3$ ligand. Higher ratios of mono-/disubstitution were usually favored by the more bulky ligands $AsPh_3$ and $SbPh_3$. Phosphites in general required a larger amount of $LiAlH_4$ or $NaBH_4$ for substitution to occur (e.g., 0.5 mmol $LiAlH_4$/1.5 mmol $Fe(CO)_5$), substitution by triphenyl phosphite was noticeably slower than substitution with other ligands. Premixing the neutral ligand with $LiAlH_4$ had a negligible effect on both the substitution rate and the product ratio.

Promoting disubstitution. The concentration effects of metal hydride and ligand were additive at least in part as shown in Table 2. Increased concentrations of both metal hydride and ligand favor disubstitution. $Fe(CO)_3(PPh_3)_2$ was isolated in good yield (71%) when the larger amount of $LiAlH_4$ was added over a period of time. It appears likely that the disubstituted product arises via eqn. 2 since $Fe(CO)_4L$ could be converted to $Fe(CO)_3L_2$ under the same conditions. We have not yet succeeded in applying this sequence satisfactorily to the synthesis of unsymmetrically substituted complexes of the type $Fe(CO)_3LL'$. In most cases the crystalline disubstituted iron carbonyl complexes were less soluble than the monosubstituted complexes and, therefore, the former was easily purified by recrystallization.

Observations on the mechanism. Although we cannot suggest a mechanism for the substitution, certain observations are reported and discussed as they relate to a possible mechanism. Seemingly, the first possibility to be explored would be that shown in Scheme 1. $Fe(CO)_5$ is susceptible to nucleophilic attack on CO by strong nucleophiles [13]. The formyl complex I and the hydride complex II are both known and I has been reported to undergo slow (at 25°C) decarbonylation (eqn. 4) to the hydride II [12]. However, several observations as cited below suggest that the hydride and formyl complexes are unlikely intermediates in the substitution reaction.

SCHEME 1

$$Fe(CO)_5 + H^- \rightleftharpoons \underset{(I)}{HCOFe(CO)_4^-} \qquad (3)$$

$$HCOFe(CO)_4^- \rightleftharpoons \underset{(II)}{HFe(CO)_4^-} + CO \qquad (4)$$

$$HFe(CO)_4^- + L \rightleftharpoons HCOFe(CO)_3L^- \qquad (5)$$

$$HCOFe(CO)_3L^- \rightarrow H^- + Fe(CO)_4L \qquad (6)$$

No intermediates were detected by infrared spectroscopy suggesting that the intermediates involved were quite reactive under the usual reaction conditions. In separate experiments the hydride complex II was prepared both as the isolated bis(triphenylphosphine)iminium salt and as the lithium salt in situ and was treated in each case with $P(CH_2CH_2CN)_3$ There was no conversion to $Fe(CO)_4L$

Iron pentacarbonyl fails to react with L by itself but it does react with $LiAlH_4$. At the low concentrations of $LiAlH_4$ used to promote monosubstitution (e g 0 125 0 50 mmol $LiAlH_4$/1 5 mmol $Fe(CO)_5$) there is little reaction between the two reagents in the absence of L If the $LiAlH_4$ concentration is increased (to 1 25 mmol/1 5 mmol $Fe(CO)_5$), a rapid reaction takes place (even in the presence of L) in which approximately 1/2 to 2/3 of the $Fe(CO)_5$ is converted to other carbonyl products The dark red solution obtained from this reaction appeared to contain three carbonyl products in addition to unreacted $Fe(CO)_5$ and we tentatively label these products as the formyl complex I, the hydrido complex II, and a polynuclear carbonyl complex (to which we ascribe the red color of the solution) Addition of a neutral ligand to the red solution and heating in a 75°C bath resulted in the conversion of unreacted $Fe(CO)_5$ to $Fe(CO)_4L$ but the other carbonyl products, derived from the action of $LiAlH_4$ on $Fe(CO)_5$, remained unchanged Thus, it appears unlikely that the hydride and formyl complexes are involved in the substitution of $Fe(CO)_5$ other than as minor byproducts and that Scheme 1 as written represents an unlikely path for the substitution of iron pentacarbonyl

This work has demonstrated the utility of $LiAlH_4$ and $NaBH_4$ for promoting the substitution of $Fe(CO)_5$ by a variety of neutral ligands under relatively mild conditions The extent of substitution can be controlled by choosing appropriate concentrations of starting materials This simple one flask synthesis is particularly useful for the preparation of frequently hard-to obtain mono substituted iron carbonyl complexes

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